The Chemistry of Cements.
THE STOCKHOLM SYMPOSIUM.

THE international meeting on " The Chemistry of Cements " held in Stockholm from July 6 to 8, formed a landmark in the history of scientific research on hydraulic cements. This congress, which was organised by the Royal Swedish Institute for Engineering Research and the Swedish Cement Association, attracted authorities from many different countries and its organisers are to be congratulated on a unique and successful meeting.

The Symposium was opened by Professor A. F. Enström, President of the Royal Swedish Institute for Engineering Research, and following this an address of welcome was given by Consul W. de Shärengrad, President of the Swedish Cement Association. The remainder of the morning was occupied by two introductory lectures. In the first, by Professor The Svedberg of the University of Upsala, on " The Study of Giant Molecules by Means of Ultracentrifugal Sedimentation, Diffusion, and Electrophoresis," an interesting account was given of the experimental methods used in the well-known work which gained for the lecturer a Nobel prize. The second lecture, by Professor Hedvall of the Chalmers Technical University, Göteborg, on " Reactions between Substances in the Solid State with Special Regard to Systems Containing Silica," provided a valuable summary of the experimental work which he has carried out in a field which is closely allied to that of cement chemistry. The remaining sessions were devoted to the presentation and discussion of the papers submitted, the chair at these sessions being taken in turn by Professor T. Thorvaldson (Canada), Dr. W. Eitel (Germany), Dr. F. M. Lea (Great Britain), Professor P Schläpfer (Switzerland), and Dr. R. H. Bogue (U.S.A.). The Secretary of the Congress was Mr. S. Giertz-Hedström, head of the cement laboratory of the Royal Swedish Institute for Engineering Research. The papers presented were as follows :

" Constitution of Portland Cement," by Dr. R. H. Bogue (Portland Cement Association Fellowship, Bureau of Standards, U.S.A.) ;

" X-rays and Cement Chemistry," by Dr. W. Büssem (Kaiser-Wilhelm Institut für Silikatforschung. Germany) ;

" Calcium Aluminate and Silicate Hydrates," by Mr. G. E. Bessey (Building Research Station, Great Britain) ;

" The Complex Calcium Aluminate Salts," by Mr. F. E. Jones (Building Research Station, Great Britain) ;

" Portland Cement and Hydrothermal Reactions," by Professor T. Thorvaldson (University of Saskatchewan, Canada) ;

" Reactions of Portland Cement with Water " by Professor P. Schläpfer (Technische Hochschule, Zurich, Switzerland) ;

" The Chemistry of Accelerators and Retarders," by Dr. L. Forsén (Skanska Cementaktiebolaget, Limhamn, Sweden) ;

" Constitution of Aluminous Cement Clinker," by Dr. N. Sundius (Swedish Geological Survey) ;

" Reactions of Aluminous Cement with Water," by Dr. G. Assarsson (Swedish Geological Survey) ;

" Chemistry of Pozzolanas," by Dr. F. M. Lea (Building Research Station, Great Britain) ;

" Physical Structure of Hydrated Cements," by Mr. S. Giertz-Hedström (Royal Swedish Institute for Engineering Research).

An additional paper on the programme, by Dr. H. E. Schwiete (University of Frankfurt/Main, Germany), on " Thermochemistry of Portland Cement Compounds " could not be presented owing to the illness of its author, but it is hoped that the paper will appear in the proceedings of the congress. The papers and discussions will be published by the Royal Swedish Institute for Engineering Research, Grevturegatan 14, Stockholm 5, Sweden.

At the first afternoon session the congress paid tribute to the memory of the famous French scientist, Henry le Chatelier, in the following telegram sent to the Sorbonne, Paris, where much of his outstanding work was done, *A l'occasion du " Symposium on the Chemistry of Cements" tenu à Stockholm le 6-8 Juillet sur invitation de l'Académie Royale des Sciences Polytechniques et de la Société Suédoise du Ciment les participants au Congrès, venus d'Allemagne, d'Angleterre, de Belgique, du Canada, du Danemark, des Etats Unis, de Finlande, de Norvège, de Pologne, de Suède et de Suisse sont heureux d'accomplir un devoir de profonde reconnaissance en rendant hommage à la mémoire du grand savant français Henry le Chatelier, qui par son génie a tant contribué à la prospérité de la Science chimique et de la Technique en frayant spécialment la voie à la Chimie des Ciments par ses travaux proéminents et fondamentaux.*

Before the congress, visits were made to cement works of the Skanska Cementaktiebolaget at Limhamn and Hellekis, the Siporex lightweight concrete factory at Dalby, the Lidköpings porcelain factory, and three concrete dams and power plants on the Göta river, the most recent of which had been constructed with a low-heat Portland cement.

Though chemical problems relating to cements have been discussed at meetings of many societies both here and abroad, no international discussion has taken place since that on "The Setting of Cements and Plasters" held in London in January 1918 by the Faraday Society. The Stockholm meeting, far wider in scope than its predecessor, indicated the far-reaching advances in knowledge that have been made in the intervening twenty years. A glance at the papers presented at the 1918 and the present meetings is sufficient to show how far carefully ascertained experimental facts have now superseded the rather vague and tentative theories current at that time. It is true that the work of Rankin and Wright on the system $CaO-Al_2O_3-SiO_2$, followed by the work of Bates at the Bureau of Standards, had resulted in the identification of the silicate compounds in Portland cement, but their conclusions had not at that time met with the general acceptance which was to come later. Some limited knowledge existed concerning the hydrated calcium silicates and aluminates, but it went little farther than the much earlier work of Le Chatelier. The study of the hydration of the anhydrous calcium aluminates and silicates had been considerably advanced by Bates and his associates, and the relative cementing qualities of the different compounds were known. Many of the subjects discussed at the 1938 meeting were, however, so far unknown as to pass unmentioned.

Within the limits of the present review, it will not be possible to discuss the papers presented in detail, but only to touch on some of the more important points which emerged. This will, however, it is hoped, be sufficient to draw attention to the forthcoming publication of the proceedings of this meeting, which should be in the hands of all who are interested in cement chemistry.

Constitution of Portland Cement Clinker.

The constitution of Portland cement clinker is a problem which has attracted workers in many different countries. After the initial studies of Le Chatelier and Torneböhm, carried out before the end of the last century, little real advance was made until phase equilibrium studies were commenced at the Geophysical Laboratory of Washington resulting in 1915 in the publication of Rankin and Wright's now classical paper on the system $CaO-Al_2O_3-SiO_2$. Later work on other systems, amongst which may be particularly mentioned various ternary systems containing ferric oxide, alkalis and magnesia investigated at the Bureau of Standards, and the quaternary system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ published from the Building Research Station in 1934, has led to a clear picture of the nature of most, though not all, of the crystalline components in cement clinker. Thus the presence of the compounds $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ is now well established; magnesia it is known can be present as free MgO, but there is still some doubt concerning the nature of the alkali compounds. The assumption that Portland cement clinker could be regarded entirely as a product resulting from an equilibrium crystallisation of the mix was, however, called in question in 1933 by Forsén who pointed out that under commercial conditions of production the time available during cooling was pro-

bably insufficient for equilibrium to be established and some type of arrested equilibrium was to be anticipated.

From their investigation of the system $CaO-Al_2O_3-SiO_2-Fe_2O_3$ Lea and Parker were able to show that at clinkering temperatures the crystalline solids present in a cement mix were the tri-calcium and di-calcium silicates, and that from 20 to 30 per cent. of liquid, the amount depending on the mix composition and burning temperature, was formed. As the composition of this liquid could be obtained from the phase equilibrium data it was possible to calculate the compound composition of the cooled clinker assuming the liquid crystallised without reaction with the pre-existing crystalline silicates, or that it became supercooled and formed a glass. In this way it was possible to apply corrections to the earlier formulæ given by Bogue in which the compound content of clinker was calculated on the assumption of complete equilibrium crystallisation. This work had led to intensive studies in a number of laboratories on the formation of glass in commercial clinkers and to its effect on the properties of the resultant cements. An excellent summary of this most recent work was given by Bogue in the paper presented to the congress, while notable contributions to the discussion were made by Eitel, Parker, and Swayze.

The further development of the technique for the preparation of thin sections of clinker, of etched and polished surfaces for examination by reflected light, and of polished and etched thin sections which can be examined by both transmitted and reflected light, has in the hands of Insley, Parker, Tavasci, and Ward led to notable advances. By differential etching of the clinker matrix, i.e. that part of the clinker which was liquid at the clinkering temperature, the crystals of MgO, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$, and the glass can now be differentiated in favourable cases, but there still remains one serious difficulty since the etch reaction of the glass is found to vary considerably with the ratio of its alumina : ferric oxide content. One particularly interesting point in the application of this work has been the finding by Bogue and his co-workers that, when appreciable amounts of magnesia (more than about 2 per cent.) are present in cement in the crystalline form as periclase, long delayed expansion may occur in use, but that when the magnesia is retained in the glass considerably higher contents cause no similar unsoundness. This has led in the U.S.A. to the adoption of an autoclave high-pressure steam soundness test for cements to detect latent unsoundness arising from the presence of too high a content of crystalline magnesia.

Two methods have been developed for the determination of the amount of glass in Portland cement clinker, but neither at present is sufficiently accurate to yield more than a rough estimate. One method depends on microscopic counts on etched specimens, but there are still uncertainties in the differentiation of glass from $3CaO.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$. The other method is a thermochemical one in which the heat of solution of a clinker is determined, and a duplicate specimen annealed until crystallisation of the glass is complete and the heat of solution again determined. From the difference between these

heat of solution values, and a knowledge of the latent heat of crystallisation of the glass, the glass content is calculated. Certain assumptions involved in the method reduce its accuracy, but it is considered by Bogue that the error should not exceed ± 5 per cent.

Further evidence was put forward in discussion by Eitel, confirming earlier work, that tricalcium silicate can take up tricalcium aluminate in solid solution to a very limited extent—some few per cent.

X-Rays in Cement Chemistry.

The application of X-ray methods to cement problems may be said to have had two main objects, the one the more utilitarian purpose of providing an additional means for detecting and estimating the various compounds present in cement clinker and in hydrated cements, the other the more fundamental purpose of determining the structure of these compounds and why they have cementitious properties, and also how the various hydrated compounds are related one to another. The minimum amounts of the various clinker compounds which must be present before they can be detected by X-ray methods are now known, though with future improvements in technique some reduction in these minimum values may become possible. The study of the structure of the compounds leads at once into intricate and very specialised fields and it must suffice to say that in his paper Dr. Büssem has given a summary of the data at present available which will be invaluable to those working on this subject.

Hydration of Cements.

There are probably few aqueous systems which are more complex and difficult to study than those involved in the hydration of cements, including as they do the hydrated calcium silicates and aluminates ; the additional components involved when accelerators and retarders are introduced and the complex calcium aluminate compounds of the type of the calcium sulphoaluminates are formed ; and the very different reaction products obtained when cement compounds react with steam under high pressure instead of with water. The papers on these subjects presented by Bessey, Forsén, Jones, Schläpfer and Thorvaldson contain a body of knowledge which will remain a lasting tribute to the work done during the last ten years, even though final agreement has on some points still to be reached.

At one of the official dinners Dr. Forsén told us that his interest in these problems started when he asked himself the question, " Why gypsum ? " We may repeat, " Why gypsum as a retarder for Portland cement ? " In this spirit, that which underlies all research, Forsén, with Mylius as his assistant, first investigated the complex salts formed by hydrated tricalcium aluminate with the halide, nitrate, chlorate, iodate, acetate, and sulphate salts of calcium, work which has been extended to other salts by several investigators and summarised by Jones in his useful paper to the congress. Forsén's own contribution to the meeting, which covered the experimental work done by him and his assistants during the last few years in the study of normal and rapid setting, has resulted in a theory which links together many earlier isolated observations and presents a scheme

into which can be fitted the action of a wide variety of different substances on the setting of cements.

Briefly, when Portland cement reacts with water the components at first enter into solution in the same stoichiometric proportions as that of the anhydrous compounds. From the principal cement compound, $3CaO.SiO_2$, a solution is formed which at first contains lime and silica in the molecular ratio $3 : 1$ and from which a less basic hydrated calcium silicate—formulated by Forsén as $2CaO.SiO_2.4H_2O$—is precipitated, leaving a supersaturated lime solution. Hardening is the result of the continuous solution of the anhydrous silicate compounds and a precipitation of the hydrated compound. Normal hardening can be influenced in different ways by substances dissolved in the water with which the cement reacts. Aluminates in solution hinder the formation of the hydrated calcium silicate and give in its place a gel containing aluminium hydroxide and silica and comparatively poor in lime, leading to both quick set and to reduced strengths. In normal setting the solution formed is one in which the solubility of the aluminates is considerably reduced and the aluminates dissolved are at once deposited as films around the cement grains, thus retarding their solution. Retarders are compounds which precipitate the aluminates in this manner, while quick setting occurs when no retarding agent is present in solution or is formed directly the cement reacts with water. The detailed development of these conceptions in Forsén's hands leads, as shown in his paper, to an explanation of the effect of different salts and of the importance of the alkali content of cements. When no alkali is present quick-setting cements can be retarded by lime, but when, as in all commercial clinkers, alkalis are present, lime alone is no longer an effective retarder and the addition of gypsum is necessary. In the former case the presence of lime alone in solution is sufficient to reduce the solubility of the aluminates to a low value, but when alkalis, derived from the cement, are also present the solubility of lime is much depressed, the aluminate compounds are more soluble, and an additional agent is necessary to precipitate them from solution. This the gypsum does by the formation of the less soluble calcium sulphoaluminate. Forsén's results, which merit detailed study by all concerned with this important subject, now enable us to understand earlier partial and conflicting views such as that of Rohland that alkalis catalysed the setting of cements, of Kühl that accumulation of alumina in solution was necessary before setting would commence, and of Roller that lime is the primary retarding agent. It should also be mentioned that in Forsén's view the silicate compound formed is sub-micro crystalline and hence it can be deduced that normal setting leading to good strength development is a crystallisation phenomenon, as originally postulated by Le Chatelier, while rapid setting, associated with a lower strength development, is the result of a gel formation—the theory advanced by Michäelis to explain the whole setting and hardening of cements.

The compound $3CaO.Al_2O_3.3CaSO_4.31H_2O$, now commonly termed the high-sulphate form of calcium sulpho-aluminate, has been known since the work of

Candlot some forty years ago and has been prepared by numerous later investigators. For a period it was often called by the very misleading expression " the cement bacillus " because it is formed during the destructive action of sulphate salt solutions on mortars and concretes. The compound $3CaO.Al_2O_3.CaSO_4.12H_2O$, known as the low-sulphate form of calcium sulphoaluminate, was described by Lerch, Ashton, and Bogue in 1929, but, as it could only be obtained from solutions of high-hydroxyl ion content, it has generally been assumed that in the reaction of gypsum during the setting of cement the high sulphate form is produced. The evidence now put forward by both Schläpfer and Forsén suggests, however, that this assumption is incorrect and that actually it is the low sulphate form of calcium sulphoaluminate which is produced during the setting of cements containing normal contents of gypsum. In the light of the data supplied by Forsén, showing how considerably the solution in contact with setting cement may become supersaturated with lime, this is perhaps not altogether surprising. It would not, however, be safe at present to conclude that the low sulphate form is always produced during the setting of cement for, as Jones points out, a high-calcium sulphate concentration and lower temperatures tend to favour the formation of the high-sulphate form while a high lime concentration and higher temperatures tend to cause the low-sulphate form to separate from solution. It is possible, therefore, that the conditions existing during the setting of cement may be near the critical limit and that differences in the relative rates of solution of the cement compounds and the gypsum, or changes in temperature, may cause one or the other of the calcium sulphoaluminates to form. This is admittedly only a presumption, but it is one which it is hoped will be tested.

The composition of the hydrated calcium silicate formed during the hydration of Portland cement was discussed in the papers of Bessey, Schläpfer, and Forsén, and no definite agreement can be recorded. Bessey suggests the formula $3CaO.2SiO_2.aq$ and Forsén $2CaO.SiO_2.4H_2O$, while Schläpfer's data indicated the former compound to be formed in the hydration of Portland cement and the latter during hydration of tricalcium silicate. A definite decision is difficult, for while there is good evidence for the existence of Forsén's compound it is known that it is hydrolysed, liberating lime, when in contact with solutions at, or just below, saturation with lime. It is therefore possible that both conclusions are correct and that the one or the other compound may exist in set cement according to its age and to the temperature and other conditions under which it was hydrated.

The systems $CaO-Al_2O_3-H_2O$ and $CaO-SiO_2-H_2O$, discussed in Bessey's paper, have each been investigated by fifty or more workers. Though many of the results are conflicting, a greater degree of agreement has progressively been reached by later work ; there are still, however, serious differences of opinion, particularly regarding the equilibrium relationships in the system $CaO-Al_2O_3-H_2O$.

Twenty years ago only one hydrated calcium aluminate was believed to exist, it being described sometimes as the tri- and sometimes as the tetracalcium aluminate hydrate. This apparent simplicity has now vanished and some eight compounds, ranging from a monocalcium aluminate hydrate to a pentacalcium

aluminate hydrate, are now considered to exist. In the case of the silicates, probably four compounds, $CaO.2SiO_2.aq$, $CaO.SiO_2.aq$, $3CaO.2SiO_2.aq$, and $2CaO.SiO_2.aq$ are formed at ordinary temperatures. At high temperatures under high-pressure steam a quite different set of silicate compounds is produced, and the discussion of these formed a major topic in Thorvaldson's paper.

When tricalcium silicate is hydrated in water, free calcium-hydroxide is split off and a less basic, apparently gelatinous, hydrated silicate results. In high-pressure steam, however, no lime is liberated and a crystalline compound $3CaO.SiO_2.2H_2O$ is formed. Similarly no less than three different crystalline hydrated dicalcium silicates can be obtained from the action of high-pressure steam on $2CaO.SiO_2$, though with water it yields a gelatinous product. In the case of the calcium aluminates, hydration in high-pressure steam leads to a greater simplicity since under this condition only one compound, $3CaO.Al_2O_3.6H_2O$, is formed. The great increase in the resistance of Portland cement mortars and concretes to attack by solutions of sulphate salts produced by curing in high-pressure steam is well known and this must, as Thorvaldson points out, be connected with the changes in the composition and physical nature of the hydration products.

Aluminous Cement.

Notable contributions to the elucidation of the constitution and hydration of aluminous cement have been made by Sundius and Assarsson, and it was appropriate therefore that the two papers on this subject presented to the Symposium should have been by these authors. Mention should also be made of the written contribution to the discussion sent by Tavasci (Italy), whose work in this field is well known and whose photomicrographs have earned well-merited admiration.

The methods available for the study of the constitution of aluminous cement are similar to those which have served so well in the case of Portland cement, namely phase equilibrium studies, microscopic and X-ray examination of the fused clinker, and separation by physical or chemical means, insofar as it is possible, of the individual clinker constituents. Aluminous cement is a much less basic material than Portland cement and its composition falls into a region of the quaternary system $CaO-Al_2O_3-Fe_2O_3-SiO_2$ which has not as yet been explored, and where, indeed, on account of the prevalence of solid solutions, the difficulty of the examination is considerably increased. From the phase relations in the ternary systems $CaO-Al_2O_3-SiO_2$ and $CaO-Al_2O_3-Fe_2O_3$ it is possible to deduce the compounds to be expected in a fully crystallised mix, even though the latter of these two systems is still not completely known in the more acidic regions. A serious complication is, however, introduced by the iron oxides which are present not only as ferric oxide but also in a lower state of oxidation.

From examination of aluminous cement clinkers it is generally agreed that, apart from the iron compounds, the major crystalline constituents are calcium monoaluminate ($CaO.Al_2O_3$), the unstable form of the compound $5CaO.3Al_2O_3$ (recent work suggests the true formula of the stable compound is $12CaO.7Al_2O_3$), dicalcium silicate ($2CaO.SiO_2$), and gehlenite ($2CaO.Al_2O_3.SiO_2$). While the

compound $3CaO.5Al_2O_3$ (formulated as $CaO.2Al_2O_3$ by Tavasci) has sometimes been reported, Sundius states that he failed to find it except in quite minor proportions.   The monocalcium aluminate is in most cases the compound mainly responsible for the cementitious properties, but this does not always hold, for Sundius cites one case in which the unstable form of the compound $5CaO.3Al_2O_3$ made up some 80 per cent. of the cement.   This unstable compound, which is easily recognised from its very characteristic pleochroism, is, in aluminous cement, probably not a pure aluminate, but contains other compounds in solid solution. The same also applies to the gehlenite in aluminous cement, and to some extent to the calcium monoaluminate.   The identification of the iron compounds is a matter of considerable difficulty, but both ferrous and ferric oxides are found by Sundius to be predominant constituents in a dark glass-like substance which from X-ray evidence probably contains crystalline free ferrous oxide (wüstite). Tavasci, however, considers that this glass-like substance is essentially magnetite (Fe_3O_4), and also states that the dicalcium silicate in aluminous cement is pleochroic and must contain other substances in solid solution.   These probably include fayalite $(2FeO.SiO_2)$, as it is known that this compound can dissolve to the extent of 10 per cent. in dicalcium silicate.   Crystalline compounds containing ferric oxide have also been detected, the calcium ferrites by Sundius, and solid solutions reported as those of $2CaO.Fe_2O_3$ with $4CaO.Al_2O_3.Fe_2O_3$ and $CaO.Al_2O_3.$-$2Fe_2O_3$ by Tavasci.   Titania is an important minor constituent of aluminous cement, occurring to the extent of about 2 per cent., and it is found to be present mainly as perovskite $(CaO.TiO_2)$ which also, however, contains other constituents in solid solution.   Part of the titania is also present in the glass-like constituent and also in solid solution in the gehlenite.

The complexity of aluminous cement clinker will be realised from the frequency with which the words " solid solution " have appeared in the foregoing account, and, though Sundius attempted in some cases to compute the content of the different compounds present, the accuracy of these calculations must at present remain doubtful.

Our knowledge of the process of hydration of aluminous cement is closely connected with that of the system $CaO-Al_2O_3-H_2O$, and the uncertainties which remain in this system are to some extent reflected in the interpretation made of the hydration process.   The principal product is thought by Assarsson to be a hydrated monocalcium aluminate gel, though the crystalline dicalcium aluminate hydrate was sometimes observed, and, if higher temperatures were employed, the cubic compound $3CaO.Al_2O_3.6H_2O$.   Other crystalline hydrated aluminates were sometimes found present in small amounts.   Liberation of hydrated alumina must also accompany the formation of any of these crystalline compounds since they originate from the calcium monoaluminate in the cement.   The gehlenite and dicalcium silicate in aluminous cement hydrate much more rapidly than the corresponding pure compounds, and this must be attributed to the presence of other components in solid solution causing an increased reactivity.   The dark glass-like constituent of the cement and the perovskite are not hydrated.

Pozzolana.

Pozzolanas, both natural and artificial, have, in recent years, been the subject of many investigations stimulated by the increased interest now taken in pozzolanic cements. Italian workers have made the largest contributions to our knowledge of natural pozzolanas, of which there is a great variety in Italy, and in the last five years a large number of papers on this subject have appeared in Italian journals. Artificial pozzolanas have interested investigators in many countries, as has also the general study of the mechanism of the pozzolanic reaction. In his paper on the chemistry of pozzolanas Lea discussed the constitution of pozzolanas and the source of the properties they show, the manner in which they combine with lime, the mechanism of their action in increasing the resistance of cements to attack by chemical agents, and means for their evaluation.

Knowledge of the chemistry of pozzolanas is less advanced than that of, for instance, Portland cement, and there are still many problems on which further investigation is required. Thus while there was evidence that the compound $3CaO.2SiO_2.aq$, or its solid solution with $CaO.SiO_2.aq$, and also the aluminate compound $4CaO.Al_2O_3.aq$, are formed in the reaction of pozzolanas with lime, there was no information available as to the possible formation of hydrated alumino-silicates. In his paper on " X-rays and Cement Chemistry," and in a contribution to the discussion, Büssem stated that very recent work had provided evidence for the existence of two such compounds, $2CaO.Al_2O_3.SiO_2.aq$ and $3CaO.Al_2O_3.2SiO_2.aq$. Until further knowledge is available as to the conditions under which these compounds can be formed and remain stable, the question of their formation in the setting of Portland cement, and in the reaction of pozzolanas with lime, must remain open, but it seems that some revision of the present conceptions of these actions may be required.

Probably the most common reason for the use of pozzolanas in cement mixes is the increased resistance to attack by chemical agents, and in particular by sulphate salts, which is thereby obtained, but the mechanism of this action is by no means clear. The compounds formed by the combination of pozzolanas with lime are not inert to attack by sulphate salts, though they are considerably more resistant than some of the compounds present in hydrated Portland cement, and it is therefore questionable if this factor alone provides a full explanation. A Rumanian worker, Steopoe, has during the last few years suggested that the primary cause of the increased resistance is to be found in the production of gelatinous silica from pozzolanas. According to this theory the attack of aggressive agents on set cement, or pozzolana-lime compounds, results in the removal of lime and the formation of alumina and silica gels. Though alumina gel has little or no bonding power, silica gel can form a good cement and in Steopoe's view the addition of pozzolanas increases the amount of the bonding silica gel produced as the original set cement compounds are decomposed and their cementing power lost. Though Steopoe has advanced considerable evidence in favour of this theory there are still some serious difficulties to be overcome. Yet another theory is that of Lafuma in which changes in the mode of crystallisa-

tion of the calcium sulphoaluminate, formed by the reaction of sulphate salts with the alumina compounds in the set cement, are regarded as the cause of the increased sulphate resistance obtained by the use of pozzolanas.

The development of rapid chemical methods by means of which the quality of a pozzolana could be assessed has long been desired, but it appears doubtful if any method depending on the estimation of silica soluble in acid or alkali solutions will be obtained. Certain methods of this type have been found useful when dealing with one particular pozzolana, but when applied more widely to other pozzolanas the results have not been satisfactory. The use of free calcium hydroxide determinations on set cement, or lime-pozzolana mixes, was advocated by some investigators, though at present considerable uncertainty attaches to the absolute accuracy of the values obtained. It was stated by Lea in his paper that from the difference in the strength developed by pozzolanic cements when cured under specified conditions at 18 deg. and 50 deg. C. a good estimate of the quality of a pozzolana could be obtained.

The Physical Structure of Hydrated Cement.

Giertz-Hedström discussed one of the most difficult subjects before the congress. How is the structure of set cement built up during hydration ? How does the bonding action take place ? What is the cause of shrinkage and creep ? These are some of the questions to be answered when we consider the physical structure of set cement. It is a subject which touches the field of surface chemistry and of the forces which exist between liquids and solids. The speed of the reaction between cement and water, the volume changes which occur, the amount of water which is combined and the relation of this to the strength developed—these are amongst the topics also covered in Giertz-Hedström's paper.

Discussing the fixation of water in set cement it was suggested that as an arbitrary, but useful, measure the water retained on drying at normal temperatures in an atmosphere of 30 per cent. relative humidity should be regarded as chemically bound or surface-absorbed water, that lost to atmospheres of between 30 and 40 per cent. relative humidity as water in capillaries typical of set cement, that lost between 40 and 95 per cent. relative humidity as water in coarser capillaries, and water lost above 95 per cent. as free water. It was pointed out, however, that the calculation from the Thomson equation of the radius of capillaries which would retain water at the lower of these vapour pressures is probably quite invalid in the light of modern physico-chemical work.

The main theories of the bonding action of set cement are those of Michäelis and Le Chatelier. Michäelis's conception of cementing action as the hardening of a gel by " inner suction," that is the adsorption of water from already hydrated cement by inner cores of unhydrated cement, is difficult to conceive. Le Chatelier's crystalline theory must not be regarded as the interlocking of crystals of microscopic dimensions, but rather in terms of the surface forces between crystalline particles of sub-microscopic size. The essential silicate cementing

material appears as an amorphous mass, but if Forsén's view is accepted it must be regarded as crystalline though the crystals are of sub-microscopic size.

Set cement mortars and concrete are capillary systems, and an attempt has been made by Freysinnet to explain shrinkage and creep by variations in the negative pressure of water contained in the capillaries. This negative pressure may be regarded as the equivalent of a compressive stress, and variations in it as equivalent to changes in stress causing corresponding changes in elastic deformation. This theory must, it seems from the discussion, be regarded as invalid, for the simple classical picture of capillary condensation on which Freysinnet relied requires considerable modification, and the introduction of effects due to changes in surface energy at the solid-liquid interface. The alternative view that shrinkage and moisture movement may be attributable to changes in volume caused by dehydration and rehydration of the bonding set cement compounds has considerable support.

It was evident from the paper and the subsequent discussion on the physical structure of set cement that a wide field is open here for research and that present conceptions must be regarded only as a framework to be filled in and modified as further investigations are made.

The foregoing account of the Stockholm meeting will, it is hoped, give at least some indication of the great progress made in cement chemistry in the last two decades and of the great value of the Symposium in indicating the stage which has now been reached and the problems remaining to be solved.

In conclusion, thanks are· due to the two Swedish institutions which organised this meeting for the service thereby rendered to the progress of cement chemistry, and also for the hospitality which accompanied it.

Design and Operation of Modern Lime Works.—XIV.*

By N. V. S. KNIBBS, D.Sc.

The Hydration of Lime.

CONTINUOUS HYDRATORS.—To these hydrators lime and water are fed continuously, with some form of control of the flow of each. The correct amount of water to be used for a given rate of lime feed is maintained either by experience coupled with inspection of the hydrate made, or by more accurate means, and particularly by control based on the temperature of the contents of the hydrator taken at a suitable point. If lime is supplied with excess water, and is agitated in a large enough vessel from which the heat losses by radiation, etc., are small, the temperature attained will depend on the amount of water used. When hydration of the lime is practically complete a temperature exceeding 100 deg. C. shows that there is not sufficient excess water to use all the heat of hydration. If, on the other hand, the temperature is more than a few degrees below 100 deg. C. it shows that there is too much water, and the hydrate produced will be wet. By maintaining a temperature close to 100 deg. C. exact hydration is assured, and by varying the temperature within a few degrees of this point any desired percentage of free water in the hydrate may be obtained.

For the success of this type of control there must be proper mixing of all the water with the lime, which must be crushed so small that there is no appreciable difference of temperature between the outside and the inside of the pieces. Moreover, the water must all be added at once—not sprayed in at widely different points—otherwise it would be possible to have " burning " of the lime even when the measured quantity does not exceed 100 deg. C. For example, if part of the water is added as the lime enters the hydrator and the rest is mixed in farther along the hydrator but before the point at which the temperature is measured, the temperature may reach a high level and the lime be " burnt " before the point at which the secondary water is added, and adjustment of the latter to keep the measured temperature below 100 deg. C. would not undo the harm done. It is also necessary to have a sufficient bulk of material in the hydrating vessel and at the point of temperature measurement, and to have sufficient agitation. If there is not an adequate mass of reacting material the temperature fluctuations are too rapid for adequate hand control of the water supply (although automatic control could be employed successfully), and in addition the heat losses from causes other than evaporation tend to be too great, which decreases the reliability of the temperature as a means of control.

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* Previous articles in this series appeared in our issues for January, February, March, April, May, August, September, October, November and December, 1937, and January, March, April, May and July, 1938.

This means of control of hydration is not relied upon in all continuous hydrators, some of which are designed to permit a large heat loss through the casing. It is then necessary to maintain correct conditions by other means, such as inspection, analysis of product, etc.

THE SCHULTHESS HYDRATOR.—The Schulthess hydrator—probably the first continuous hydrator to be manufactured—differs from nearly all others in that it is ordinarily fed with lump lime. It consists of a feed hopper, a rotary cylindrical screen or primary hydrator, a mixing cylinder or secondary hydrator, and a " condenser " or vent stack. Lump lime is fed by hand or mechanically to the feed hopper, whence it falls directly into the rotary screen where it is
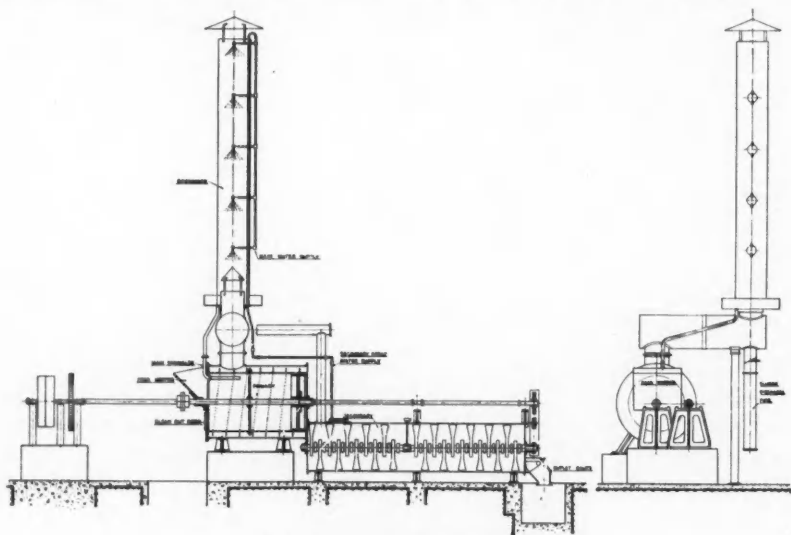

Fig. 62.—Schulthess Hydrator.

sprinkled with water from the primary water supply. As slaking commences the lumps break up, and when it is small enough the partly-hydrated lime passes through the screen to the space between the screen and the casing and thence to the hydrating cylinder, being conveyed there by a helix fixed to the periphery of the screen. The hydrating cylinder is swept by rabble arms attached to a central shaft ; these arms also serve to convey the material to the discharge end where it passes out at the outlet chute. In most of these hydrators the screen and the rabble arms are carried on one shaft and housed in the same casing, but *Fig.* 62 shows the latest type of hydrator of large capacity in which the screen is separately housed and driven. Any large pieces of unslakable lime, slow-slaking lime, and unburnt stone remain in the screen and are removed periodically at the cleaning-out door. There is a secondary supply of water to the hydrating cylinder, the water entering through one or more sprays.

Steam and dust produced in hydration pass up to the stack or condenser where they meet water from several sprays. This water as it descends is heated and becomes charged with hydrate dust, so that it issues at a collecting launder near the base as hot milk of lime, which is fed to the lime in the screen. The hydration reaction is accelerated by this hot feed.
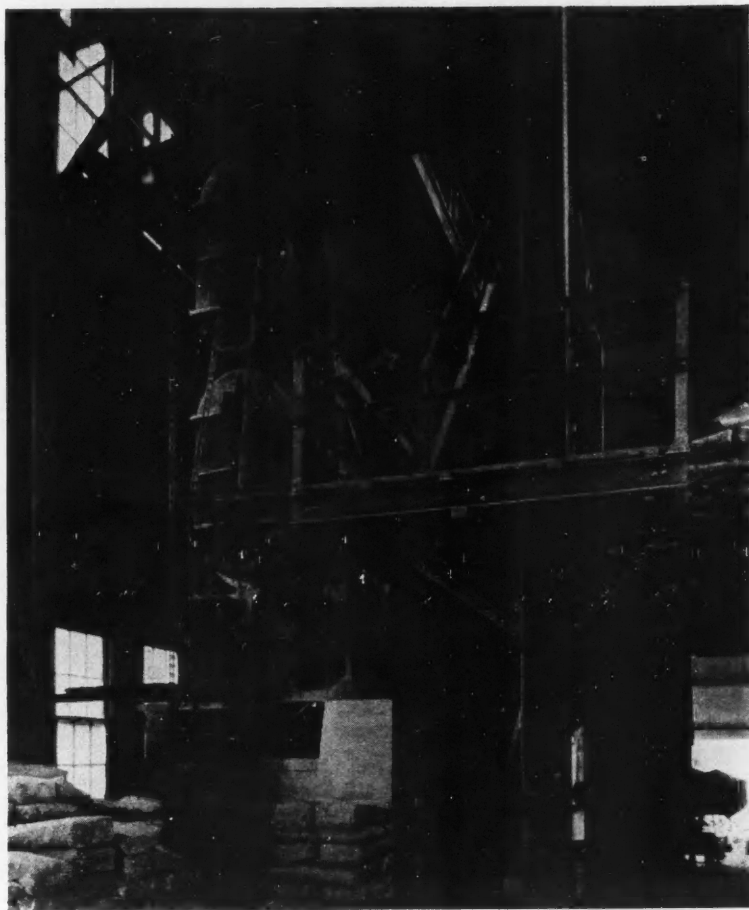

Fig. 63.—Kritzer Hydrator.

It is clear that the capacity of the hydrator is controlled primarily by the rate at which the lime when wetted will break up to a size allowing it to pass through the screen. If this is too slow, as it is in some impure and magnesian limes, the capacity of the machine is too low for it to be of commercial value.

THE KRITZER HYDRATOR.—The Kritzer is one of the earliest American continuous hydrators and it is still being manufactured and widely used there. It consists of a number, generally six, of horizontal cylinders arranged one above another and interconnected at the ends, each cylinder having a central shaft carrying stirring and conveying arms so set that they carry the material from one end of each cylinder to the other in the appropriate direction. *Fig.* 63 shows a typical six-cylinder plant. The water is sprayed into the top cylinder and the mixture passes down through the whole plant and out at the bottom.
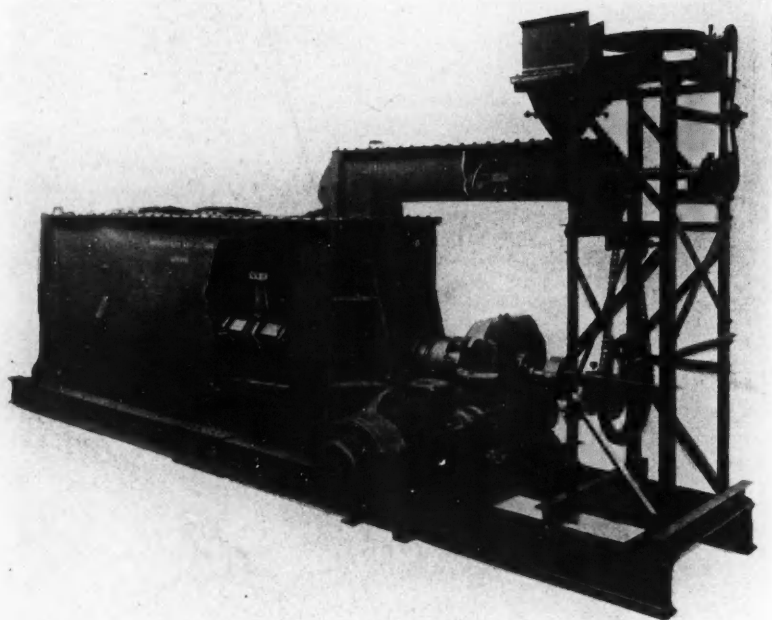

Fig. 64.—Knibbs Hydrator.

Steam and dust pass upwards counter to the flow of lime. Obviously, for its capacity, this hydrator has a large cooling surface, so that a considerable proportion of the total excess heat is dissipated there and less steam is evaporated. The overall height of the hydrator is considerable, being much more than that of most other hydrators.

THE KNIBBS HYDRATOR.—This hydrator, shown in *Fig.* 64, embodies a feeder, generally of the rotary-table type, a pre-mixer, and the hydrator proper. The pre-mixer, which is the upper small trough shown in *Fig.* 64, is a rapidly-revolving mixer where the crushed lime and water are rapidly and thoroughly

mixed together. The mixture falls into the hydrator, which is a relatively large, short, trough-shaped vessel with inspection and access doors, but completely closed. In it the lime is slowly mixed and turned over by cast steel rabble arms carried on a heavy shaft which revolves in roller bearings carried on the heavy cast-iron end frame, and which is driven through totally-enclosed worm reduction gearing. The outlet of the hydrator is an adjustable weir in the discharge end casting, over which the hydrate flows, passing thence down a chute to the plant for its subsequent treatment. There is also a discharge valve at the lowest
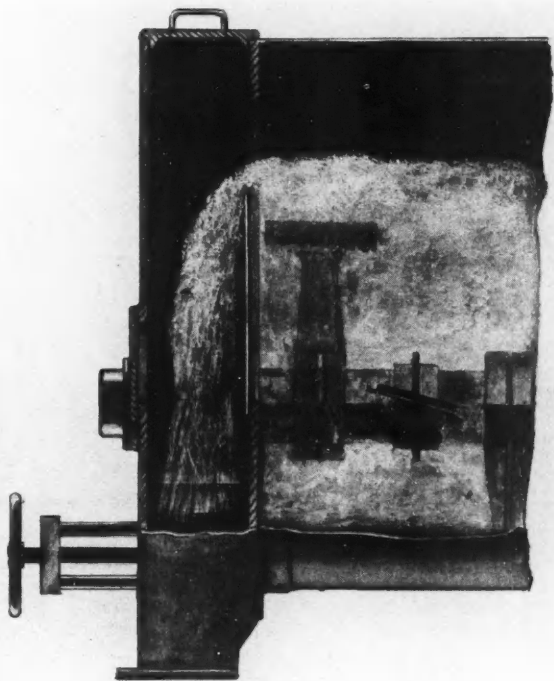

Fig. 65.—Knibbs Hydrator : Overflow Weir.

point for emptying the machine at the end of a run. A large exhaust pipe, not shown in the illustration, carries the steam and dust to a washing plant where all the dust is washed out and where the water used for hydration is pre-heated, generally to about 90 deg. C. The washing plant consists of a washing fan (which places the whole system under slight suction and thereby renders the whole plant dustless), a circulating pump, a spray eliminator, and accessories. Clean cold water from the ordinary supply passes first through a flow meter, then to the washing plant, and finally, as hot milk of lime, to the pre-mixer.

Apart from the washing plant there are two special features, namely, the pre-mixer and the overflow weir. The pre-mixer plays an important part in uniformly wetting all the lime with an excess of hot water before it passes into the main body of the hydrator, where, being less violently agitated and being surrounded by more or less hydrated material, it might fail to secure its full amount of water. The action of the adjustable weir is shown in *Fig.* 65. Its height depends to some extent on the lime, but ordinarily the machine is filled to a height just above the paddles. As the lime hydrates the light flocculent hydrate rises to the top and overflows at the weir, whilst the unhydrated or partly-hydrated lime, being relatively dense, tends to remain in the lower parts of the hydrator until it is fully hydrated. The machine therefore automatically differentiates between quick and slow slaking pieces, discharges the quick-slaking lime rapidly, and retains the slow-slaking lime for a long period whilst maintaining it at 100 deg. C. by the heat of reaction of the better lime.

OTHER HYDRATORS.—There are many other continuous hydrators which are being or have been used in the past.

The Schaffer hydrator consists of a vertical cylinder with horizontal trays and a vertical shaft carrying rabble arms stirring the material on the trays. It closely resembles a pyrites burner of the Herreschoff type. Lime and water are fed into the top tray, stirred and conveyed by the rabble arms, and pass alternatively inwards or outwards on the trays to the bottom of the machine where the material is discharged.

The Jameson " batch-continuous " hydrator contains a measuring bin for the ground lime, a measuring tank for the water, a pre-mixing chamber where lime and water are mixed in batches, and a hydrating chamber consisting of a large trough mixer. The lime and water are measured and mixed intermittently, but the hydrating chamber operates and discharges continuously.

The Kuntz hydrator is a horizontal cylindrical mixing vessel to which is attached a washing stack somewhat similar to that used in the Schulthess hydrator.

" **Ageing " or " Maturing " Hoppers.**—A frequent practice in the hydration of lime is to discharge the material from the hydrating machine to a so-called maturing silo, where the hydration reaction is supposed to complete itself. It is usual to leave the material in the silo at least overnight. Since the material remains stationary in the silo it cannot benefit by water held in surrounding hydrate except very slowly, and consequently only small particles of lime which contain sufficient excess water can be completely hydrated by this kind of treatment. Unless the lime discharged to the silo is nearly completely hydrated the expansion on hydration in the silo will make it very difficult to discharge from it, and this is one of the prime difficulties in the use of maturing hoppers. In other words, they are effective only when they have comparatively little work to do.

The term " ageing " or " maturing " bunker suggests that its purpose is to change hydrate from an unsound to a sound condition, but if it is employed in the usual manner, that is to say, taking hydrate immediately from the hydrator and discharging it to the subsequent separation plant, it does not function in this way. Ageing silos in fact, as ordinarily used, serve merely to supplement the hydrating machine.

The Hydration of Magnesian Limes.—Magnesian lime on hydration behaves in much the same way as high-calcium lime as long as it is not overburnt, but the magnesia does not combine with water, or only a small proportion of it hydrates. The amount of water required is therefore much less and the heat evolved, and therefore the water evaporated, is much less than with the same quantity of a high-calcium lime. On account of the ease with which magnesian limes are overburnt the material to be hydrated frequently contains slow-slaking pieces, and for this reason it has been usual to age magnesian limes between the hydrating machine and the subsequent separation treatment.   They are, too, better adapted to this method of treatment than most other limes because for a given absorptive capacity they require less water, and will therefore absorb more nearly the quantity required for hydration than a high-calcium lime.   Nevertheless, magnesian limes are treated with equal success in plants used for pure lime when the plants are adapted to the slower rate of reaction and the less steam evolution.   They are preferably treated in the types of plant in which the water is pre-heated to a high temperature.

Hydraulic Limes.—Hydraulic and semi-hydraulic limes differ from pure lime in that they are slower to hydrate, contain less hydratable calcium oxide, and contain calcium silicate and aluminate which are susceptible to hydration but which must not be hydrated, otherwise the hydraulic set of the lime is lost. Semi-hydraulic limes such as those made from the grey chalk, if properly burnt, are readily hydrated and, because ample heat is evolved, it is easy to hydrate the calcium oxide completely without losing hydraulicity, provided the system of control of hydration is adequate. The eminently hydraulic limes vary considerably in their properties. Some hydrate with enough heat to evaporate excess water, and they may be hydrated in plants of the usual type adapted to the conservation of the heat and to the efficient pre-heating of the water so that the commencement of the reaction is not delayed. Others are so slow in their reaction that they can be hydrated only by wetting followed by long storage in silos. Even then complete hydration is seldom assured and it is necessary to grind the product very finely so as to avoid the presence of lumps of hard-burnt unhydrated lime in the product. However, in modern continuous plant many eminently hydraulic limes may be hydrated successfully and produced in finished form immediately, whilst the unhydrated residues may be ground to produce a product similar to the " grappier " cements used in France and elsewhere. For a low " general expansion " test, however, it is desirable to mature the separated hydrate (not the crude hydrate) for a day or two in a storage bunker.

The hydrator illustrated in Fig. 62 is supplied by Edgar Allen & Co., Ltd., and that illustrated in Figs. 64 and 65 by the Sturtevant Engineering Co., Ltd.

Expansion of Cement in the Autoclave Test.

SOME interesting views on the autoclave test for cement have been given by Mr. H. H. Vaughan, of Montreal, who is intimately connected with the cement industry in Brazil. Mr. Vaughan states: Both expansion tests and microscopical examinations of cements to which hard-burned magnesia has been added are misleading in determining the action of magnesia present in the mix. There is no experimental evidence supporting the theory of abnormal delayed expansion caused by magnesia. The tests of Dr. A. H. White, the expansion tests of the American Portland Cement Association, and those quoted on high-magnesia cements agree quantitatively on the expansion that actually occurs and show a small but definite increase in water storage, while air storage tests submitted show a practically equal decrease in air storage. That no trouble develops from expansion or other effect is supported by years of experience with cement having a magnesia content higher than that allowed by U.S. Specifications. The reversal in air storage from contraction to expansion which has been shown to lead to disintegration after several years is caused by delayed expansion due to hard-burned lime and is probably the cause of the majority of failures that can be definitely allocated to the quality of the cement.

The autoclave test determines the presence of free lime that remains unhydrated after the preparation of the specimen. The explosive nature of the rapid hydration by high-pressure high-temperature steam is more noticeable than the slower expansion in the Le Chatelier test, but with regard to the determination of objectionable amounts the results are comparative. In both tests information is obtained that cannot be determined by chemical analysis.

The autoclave test is of no value in determining the magnesia content of a cement as that is obtained from the chemical analysis. It is exceedingly sensitive to variations in the burning temperature or rate of cooling of cements containing over 2 per cent. of magnesia, but does not distinguish between expansion caused by such variations or that caused by the presence of hard-burned lime ; neither does it determine whether such variations have existed in the case of cements with low magnesia contents. These objections do not apply to the Le Chatelier test, which is not affected by the magnesia. Apparently the effect of these variations if deleterious is reflected in the physical properties of the cement.

Provided the free lime content is low, a low-magnesia cement will apparently pass the autoclave test irrespective of burning conditions, rate of cooling, or proportion of tricalcium aluminate. For a high-magnesia cement (plus 2 per cent. or 3 per cent.) to pass this test the burning temperature must be high and, if the results of Lerch and Taylor are correct, higher than that which develops the best physical results, and the clinker must be cooled below a maximum rate ; the last two conditions both affect the economy in fuel consumption, the life of the lining, the cost of grinding. The proportion of the tricalcium aluminate must be kept down, which in many cases can only be accomplished by an increase

in the iron content irrespective of whether this is a desirable modification in the quality of the cement. These requirements are not imposed to improve the quality of the cement, but to enable it to pass a test in which it is submitted to conditions which it can never encounter in service and which have yet to be shown to determine the results the cement will give in use.

One point appears definite, namely that high autoclave expansion caused by these kiln and cooler variations indicates that the magnesia is exposed to more rapid hydration. It cannot be converted from the dense-burned to the hard-burned form by slow cooling or low burning temperature. Exposure to more rapid hydration must result in less unhydrated magnesia after any given time and the inference that autoclave expansion due to this cause is an indication that delayed expansion will occur is entirely unjustified.

Low expansion in the autoclave tests determines that, so far as unhydrated lime is concerned, the cement is of satisfactory quality ; so does the Le Chatelier test. High expansion in the autoclave test does not determine that the cement is of unsatisfactory quality ; in the Le Chatelier test it does. It would certainly have appeared more reasonable when condemning the pat test as unsatisfactory to have considered the possibilities of a well-established test that has proved reliable and satisfactory for years than to have adopted an extreme type of test without thoroughly investigating its action under all conditions. The present limits allowed in the Le Chatelier test are perhaps liberal, but even as they are it would prove sound policy to ascertain whether any cement that has passed this test has ever given trouble in service before resorting to a test in which the cause of its indications are so indeterminate.

That the autoclave test is valuable for plant control may be freely admitted, and if it were introduced for a particular quality of cement there could be no possible objection. If applied to all cements made, and especially to cements when freshly ground, undoubtedly batches will be produced which do not comply with its requirements and the question must arise as to what is to be done with that cement.

With regard to lime the situation while similar presents certain differences. It appears to occur in the amorphous form which hydrates rapidly and may be termed quick lime, and in the crystalline or hard-burned form which hydrates slowly. The action of this constituent is clearly described by Lea and Desch. After referring to the amorphous form which apparently can exist in cement, they discuss the action of the crystalline form which is formed at 1,400 deg. C., the crystals continually increasing in size with time. A large crystal placed in water dissolves very slowly at the surface. Finely-powdered crystals which at first appear to be inert with water in a few minutes hydrated with explosive violence. They remark that the decrease in reactivity of the lime with increasing temperature of formation (i.e. with larger crystallisation) is due less to molecular change than to shrinkage and reduction of surface. They further remark that the expansion of defective cement is due to the slow hydration of certain of its constituents. That the expansion of the CaO is only apparent, as the volume of the slaked lime is actually less than the volumes of quick lime and the water

from which it is formed, but the mechanical outward thrust is very great. They further refer to the hydration of quick lime as being completed before setting begins and harmless, and state that cements prepared from mixes of too high lime content or insufficiently well-burned contain CaO in the dead-burned (or crystalline) form which only becomes hydrated after long exposure in water and then exhibits expansion in a marked degree.

There appear to be two causes that permit the formation of hard-burned lime, insufficient burning and defective mixing (with or without sufficiently fine grinding of the mix). With regard to the first, Kühl's statement that free lime cannot exist in cement clinker would appear to refer to a condition when the clinker is finally heated to 1,500 deg. C. and the formation of the C_3S is completed. At lower temperatures, above 1,260 deg., at which formation of C_3S commences while the C_2S is formed and has taken up all the lime it can, the remaining lime is not combined and does not enter into combination to form C_3S until higher temperatures are reached and sufficient time has elapsed for the reaction to occur. If, therefore, burning is not sufficiently complete there is every opportunity for the formation of hard-burned lime. With coarsely-ground or badly-mixed raw mix there is another opportunity for hard-burned free lime as the constituents will not enter into sufficiently intimate contact to enable the various reactions to occur. In some cases of large sticky clinker calcium carbonates have been detected, showing that while the exothermic action may have occurred in the surface the central portion of the mass has not been raised to sufficiently high temperature to complete the calcination.

While it is stated above that lime only exists in two forms, namely, quick lime which hydrates before setting begins and hard-burned lime which hydrates slowly, the latter must occur in a finely-divided form to account for expansion in either the pat or the Le Chatelier tests. While the Emley test for total free lime may not be accurate and includes quick lime, hydrated lime, and hard-burned lime in one total, it is practically certain that hard-burned lime does not occur when no quick lime is present. The Le Chatelier test may show a low expansion with high free lime, i.e. when mostly quick lime, but the Le Chatelier expansion is never high with low total free lime. High expansion in the Le Chatelier test undoubtedly indicates a danger of defective results in service. These rarely develop in water storage tests as in most cases, due to the continued presence of water, the hydration is gradually completed. Conditions in service more closely resemble those in ordinary or humid air storage, and expansion of the hard-burned lime is undoubtedly the cause of the type of abnormal expansion-shown by R. N. Young. This is accompanied by a definite reversal in the expansion curves in dry and humid air, and a similar reversal is shown in Dr. White's test in which finely-ground calcite was added to the cement. This danger signal was exposed years ago but apparently ignored by all except Mr. Young. Possibly Dr. White's remark that " Magnesia does not give trouble through expansion if the cement products are kept continuously in air " accounts for the preference for water storage, which shows very little, in place of air storage which can show a great deal. This delayed expansion is entirely different in form from any expansion

caused by magnesia, which in any event would be shown in water storage and not in air storage tests.   Fine particles of hard-burned lime are the cause of high expansion and possible deterioration during the first month or a year in water storage and very possibly an important factor if not the main cause of the deterioration shown in Young's paper (*Journ. Am. Conc. Inst.*, Vol. 9, No. 1).   It seems unreasonable that the large grains ascribed to lumps and not entering the melt should occur in such quantities or regularity as to exert an important influence in service.   For a content of 1 per cent. any size particles will be spaced on the average 10 diameters apart and this is certainly not the case with these large grains.   It is more likely that the finer particles of hard-burned lime which do not hydrate in the preparation of the test piece but will hydrate 20 microns deep in the steam test, will hydrate far more slowly in air storage and give rise to the delayed expansion.   It is significant that added hard-burned magnesia which will hydrate 20 microns in the autoclave gives rise to delayed expansion between three and eight years in water storage and is unaffected in air storage, while hard-burned lime which is hydrated 20 microns in the steam test gives rise to delayed expansion in six months to four or five years in air storage.   The two actions appear reasonably similar.

It may be noted that in each of these cements the MgO content is low, 2 · 1 per cent. to 3 · 4 per cent., and the delayed expansion is undoubtedly due to hard-burned lime.   The cement containing 3 per cent. free lime and 5 · 2 per cent. MgO, while wet storage expansion is high, there is no indication of any deterioration in service or any reversal in air storage curves.

Effect of Rate of Cooling Clinker.

A SERIES of tests has been made by Mr. Yoshiaki Sanada, of the Iwaki Cement Co., Ltd., to ascertain the effect of different rates of clinker cooling on the strength of mortar and concrete. Three clinkers of similar composition were tested, a typical analysis being : SiO_2, 23.07 per cent. ; Al_2O_3, 5.96 per cent. ; Fe_2O_3, 3.44 per cent. ; CaO, 65.93 per cent. ; MgO, 1.32 per cent. ; insoluble matter, 0.02 per cent. Samples of these clinkers were cooled in ice, water, air, and a cooling drum.

In the case of standard 1 : 3 mortars prepared in accordance with the Japanese standard specification, it was found that generally the quicker the clinker was cooled the higher the strength of the mortar at 28 days. The increases in compressive strength in kilogrammes per square centimetre at 28 days were as follows : Ice cooling, 677 ; water cooling, 670 ; air cooling, 651 ; cooling drum, 641.

The rate of cooling the clinker made little difference in the strengths of 1 : 3 plastic mortars or 1 : 2 : 4 concretes, the results being as follows in kilogrammes per square centimetre :—1 : 3 plastic mortars : Ice cooling, 265 ; water cooling, 257 ; air cooling, 278 ; cooling drums, 275. 1 : 2 : 4 concrete : Ice cooling, 275 ; water cooling, 286 ; air cooling, 288 ; cooling drum, 280.

It was noted that the strength ratios of standard mortar to plastic mortar, and of standard mortar to 1 : 2 : 4 concrete, were not constant in these tests, but the strength ratio of plastic mortar and 1 : 2 : 4 concrete was fairly constant with different cements and at various ages.

Recent Patents Relating to Cement and Lime.

Cement and Lime.

476,435. M. Vogel-Jorgensen. June 8, 1936.

Before being subjected in a state of fine subdivision to flotation for cleaning or concentration, raw materials for the manufacture of cement or lime are heated to a temperature of at least 70 deg. C. but not exceeding 350 deg. C. The heating may be carried out either before or after the material has been ground.

Porous Concrete.

480,113. C. G. F. Cavadino and Gyproc Products, Ltd. August 18, 1936.

Barium peroxide and manganese peroxide are added to cement, plaster, or the like, water is added as usual, and then a solution of chromic and hydrochloric acids is added with stirring, whereby oxygen is evolved and the mass rendered porous.

In a modification, the barium peroxide is dissolved in half the hydrochloric acid, and chromic acid and magnesium sulphate in the other half, and the two solutions are added separately to the cement, etc. In an example, $4\frac{1}{2}$ lb. of barium peroxide are dissolved in 11 gal. of water and $1\frac{1}{2}$ gal. of commercial hydrochloric acid ; 27 oz. of chromic acid and 5 oz. of manganese sulphate are dissolved in a similar amount of dilute hydrochloric acid, and the two solutions are added at the rate of 1 gal. in five minutes to 6,800 lb. of plaster.

Trade Notice.

DUST COLLECTION.—*Fans and Facts* is the title of a new catalogue issued by Messrs. Davidson & Co., Ltd., of Sirocco Engineering Works, Belfast, describing and illustrating the fans made by the company. Photographs and details are given of a number of dust-extraction installations in different industries.